



King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com



ORIGINAL ARTICLE



Chromatographic study of the organic matter from Moroccan Rif bituminous rocks

Khalihena Groune ^{a,*}, Mohammed Halim ^a, Laurent Lemée ^b,
Mohammed Benmakhlof ^c, André Amblès ^b

^a Laboratoire Physico-chimie des Matériaux, Catalyse et Environnement, Département de Chimie, Faculté des Sciences de Rabat, Université Mouhammed V-Agdal, 4 avenue Ibn Battouta, B.P. 1014, Rabat, Morocco

^b Université de Poitiers-CNRS IC2MP (UMR 7285), 4, rue Michel Brunet (Bât B27), BP 633 86022 Poitiers Cedex, France

^c Département de Géologie, Faculté des Sciences de Tétouan, Université Abdelmalek Essadi, BP. 2121 M'Hanech II, 93030 Tétouan, Morocco

Received 5 February 2013; accepted 6 October 2014

Available online 22 October 2014

KEYWORDS

Chromatography;
Hydrocarbons;
Biomarkers;
Rock Eval pyrolysis;
Bituminous rocks;
Moroccan Rif

Abstract The bituminous rocks of the Upper Cretaceous in the Moroccan Rif have been assessed and characterized in detail using organic geochemical techniques and a variety of organic geochemical parameters. The organic matter from 4 sites was studied in order to determine its thermal maturity and its depositional environments. The organic extracts (bitumens) were fractionated on silica-potassium hydroxide column according to the aliphatic hydrocarbons, acid compounds and polar compounds. Aliphatic hydrocarbons were identified by gas chromatography and mass spectrometry (GC/MS).

The distribution of the aliphatic hydrocarbon fractions, and the various organic geochemical parameters (pristane/phytane, isoprenoids/n-alkanes, CPI, $C_{27}:C_{28}:C_{29}$ regular, $C_{29}20S/(20S+20R)$, $C_{29}\beta\beta/(\beta\beta+\alpha\alpha)$, C_{29}/C_{30} hopanes and Ts/Tm) showed that the studied samples were generally mature. Two of the 4 samples appeared to be derived from source rocks deposited under anoxic conditions while suboxic to oxic conditions seemed to have been dominant for the remaining two samples. Rock-Eval pyrolysis data in addition to GC results suggested types II, III and IV kerogens for the studied samples.

© 2014 The Authors. Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

* Corresponding author. Tel./fax: +212 05 37 77 54 40.

E-mail addresses: khalihena.groune@yahoo.fr (K. Groune), halim@fsr.ac.ma (M. Halim), laurent.lemee@univ-poitiers.fr (L. Lemée), benmakhlof@yahoo.fr (M. Benmakhlof), andre.ambles@univ-poitiers.fr (A. Amblès).

Peer review under responsibility of King Saud University.

1. Introduction

Morocco is believed to rank seventh in the world for oil shale reserves. Among the three major Moroccan deposits which come up to ground level, Tangier's one (Rif region) which was discovered during the last century is less studied compared to the Timahdit (Middle Atlas) and Tarfaya (South of Morocco) sediments probably due to a lower amount in



Production and hosting by Elsevier

bituminous rocks (Nejma, 1989; Halim, 1993; Amblès et al., 1994).

Bituminous rocks are fine-grained sedimentary rocks. Lithologically, bituminous rocks cover a broad range of rocks from shales to marls and carbonates which contain a large portion of the mineral material and a little portion of the organic material (Yen, 1976). The portion of organic material is predominantly kerogen which is an insoluble material in usual organic solvents accompanied by a small fraction called bitumen ($\leq 1\%$ by weight of raw rock), soluble in usual organic solvents (Durand, 1980). This kerogen can yield a significant proportion of an oil of similar appearance to that of crude oil upon non-oxidizing heat treatment (Pyrolysis) (Peters and Cassa, 1994; Hutton, 1987).

In this work a chromatographic study of the organo-soluble fraction (bitumen) was conducted on 4 different samples of Tangier's deposit in order to obtain useful information about the structure and the characteristics of this kind of organic matter (Philp, 1982; Larter and Horsfield, 1993). In addition, the kerogen present in each sample was investigated using the Rock Eval technique.

On the whole, the present study was aimed at obtaining information about the origin and evolution of the organic matter present in the bituminous rocks of the Tangier's deposit and determining the conventional type of each kerogen and their economical potential.

2. Experimental

2.1. Sampling and studied areas

The studied samples of the bituminous rocks are located in four sites from northern Morocco (Fig. 1, Table 1). A sample

of 20 kg was collected from each station (20–80 cm depth). TA, and AA samples are from Upper Cretaceous – bituminous marls and Upper Cretaceous oil shale successively in the unity of the Melloussa–Chouamat (from Massylienne nappe of Flyschs nappes) (Durand-Delga and Olivier, 1988; Saadi et al., 1981; Filatov, 1970) (Fig. 2A). TE, BT samples are from Upper Cretaceous bituminous Phtanites in the unity of Internal Tangier and unity of Ketama – External Tangier successively (from Intrarif of External Rif) (Kornprost et al., 1980; Durand-Delga and Kornprost, 1985) (Fig. 2B and C). The four samples were subsequently crushed, homogenized and sieved to $< 180 \mu\text{m}$.

2.2. Rock-Eval

Bituminous rocks of the studied samples were analyzed using a Rock-Eval 6 Standard device (fully automated) of the Moroccan National Office of Hydrocarbons and Mines in Rabat (Jabobker, 2003, 2004). This technique was developed at the French Petroleum Institute (Espitalié et al., 1977). The crushed sample was pyrolyzed (500–600 °C) under a helium atmosphere with a programmed temperature. The pyrolysis products are quantified according to the temperature.

2.3. Flash pyrolysis (Py-GC/MS)

Flash pyrolysis has been widely used for the analysis of synthetic or natural polymers. Flash analytical pyrolysis was performed using a pyrolyser CDS (Chemical Data System) 5150 Pyroprob. About 4 mg of finely ground crude sample was placed on a $25 \times 1.9 \text{ mm}$ (id) quartz tube filled with quartz wool. The tube was then heated from 350 to 650 °C at

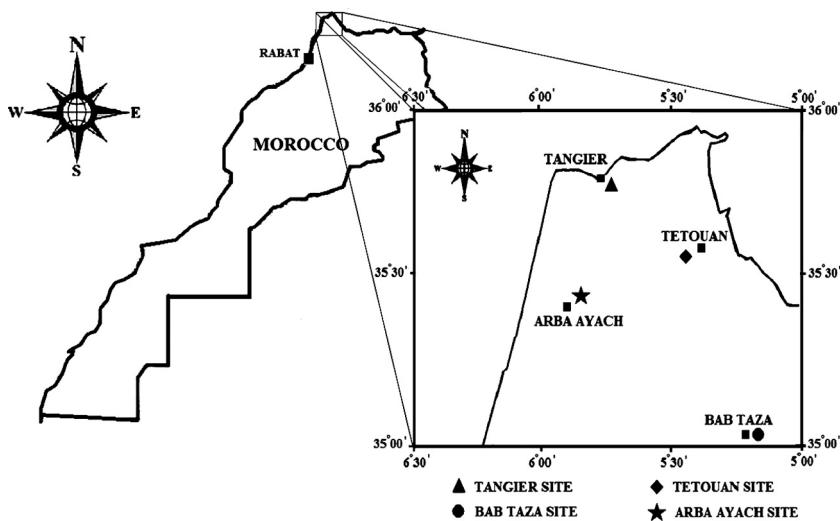


Figure 1 Study area showing the Bituminous rock sampling location.

Table 1 The coordinates of each sampling site of the sediment samples studied.

Site	Symbol of sample	Lithology	Geological age	Longitude (O)	Latitude (N)
Tangier	TA	Marl	Upper Cretaceous	$5^{\circ} 46' 33,23''$	$35^{\circ} 45' 38,07''$
Tetouan	TE	Phtanite	Upper Cretaceous	$5^{\circ} 27' 32,98''$	$35^{\circ} 33' 43,97''$
Bab Taza	BT	Phtanite	Upper Cretaceous	$5^{\circ} 10' 51,02''$	$35^{\circ} 3' 45,82''$
Arba Ayach	AA	Shale	Upper Cretaceous	$5^{\circ} 51' 05,14''$	$35^{\circ} 24' 28,54''$

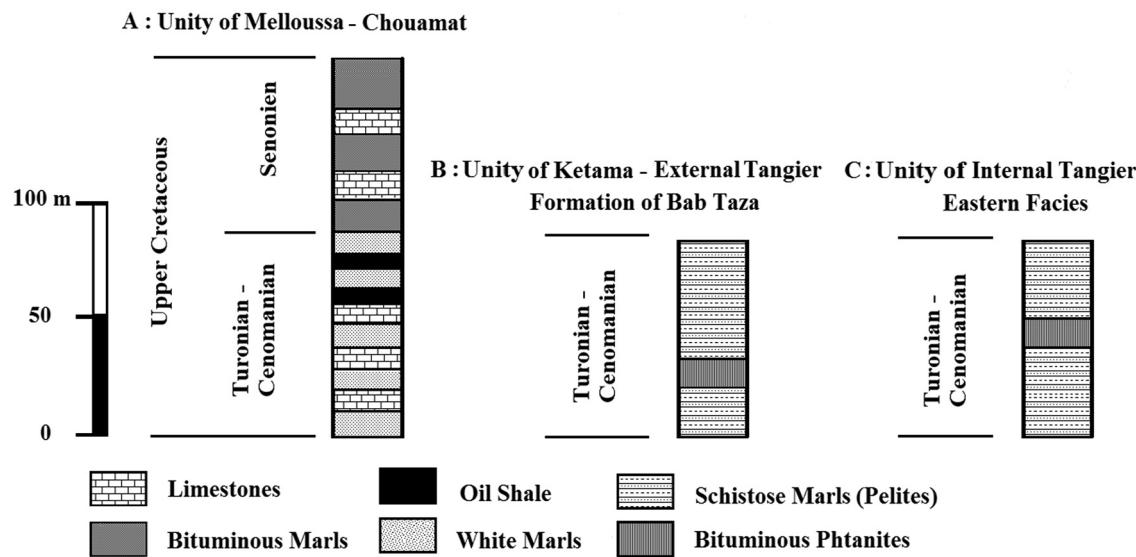


Figure 2 Stratigraphic columns of the Flysch nappes and External Rif (Marocain Rif) showing the sample position investigated (A: Durand-Delga and Olivier, 1988) (B, C: Durand-Delga and Kornprost, 1985; Kornprost et al., 1980).

5 °C ms⁻¹ and maintained at 650 °C for 10 s. Thermochemolysis products were carried into GC-MS by He gas.

GC/MS separation was performed on a Focus GC coupled with a DSQ II quadrupole using a BPX (SGE) capillary column (30 m long, 0.25 mm i.d.). Column temperature was programmed from 60 to 300 °C at a rate of 5 °C min⁻¹ and held for 30 min at 300 °C. Ionization was performed in electron impact (70 eV). The compounds were identified on the basis of their GC retention times and by comparisons of their mass spectra with those of standards and with data from the literature.

2.4. Bitumen extraction

The bituminous rock samples (<180 µm) were Soxhlet-extracted for 48 h with a dichloromethane/methanol (2:1 volume ratio) mixture. The solution was then filtered and the solvent was evaporated under reduced pressure using a rotary evaporator. The yields of total organic extracts (bitumens) are presented in Table 2.

2.5. Fractionation

The lipid extracts were fractionated on a silica-potassium hydroxide column by the method of McCarthy and Duthie (1962). After tests on TLC (Merck Kiesel gel 60F254, thickness of the silica layer is 0.2 mm, supported by a 2–3 cm layer of alumina), different fractions were collected into three fractions: neutral, acid, and polar fractions (Table 2).

2.6. Analysis of bitumens

The aliphatic hydrocarbon fractions were analyzed using gas chromatography (GC-FID) and gas chromatography/mass spectrometry (GC/MS). The analysis conditions were kept the same as mentioned above.

3. Results and discussion

3.1. Rock-Eval analysis

The total organic carbon (TOC) and Rock-Eval parameters for the bituminous rock samples are displayed in Table 3. TOC ranges between 0.45% and 4.47 %, whereas the HI and T_{max} values vary between 37 and 282 mg hydrocarbons (HC)/g TOC and 439–465 °C, respectively (Table 3) (Groune et al., 2013). According to Peters and Cassa (1994), the typical HI/ T_{max} diagram (Fig. 3) reveals the Upper Cretaceous bituminous rock sample plot in the Types II, III and IV kerogen region for AA, TA and TE, BT successively. The weak positive correlation between S₁ and S₂ for the studied samples (AA, TA and TE, BT on the one hand) (Fig. 4), suggests that the organic matter of this formation was derived from a different origin, thus supporting the data presented in Fig. 3. The T_{max} value for AA sample from the oil shale indicates that it is of early-intermediate mature oil formation stage (Table 3, Fig. 3), whereas Tmax values of the other TA, TE and BT samples are not significant due to their low S₂ hydrocarbon value (<2.5 mg HC/g rock) (Table 3) (Groune et al., 2013).

Table 2 Yields of the total extracts and fractions of bituminous rock samples.

Sample	Total extract (%) of rock	Total extract of rock (ppm) (mg _{lip} /Kg _{rock})	% Yield fraction/yield extract		
			Neutral	Acid	Polar
TA	0.307436	3074.36	3.86	0.32	95.82
TE	0.798709	7987.09	23	0.74	76.26
BT	0.936468	9364.68	51.35	3.45	45.20
AA	0.589710	5897.10	74.19	1.19	24.62

Table 3 Rock-Eval parameters of bituminous rock samples.

Sample	Parameter				
	TOC (%)	T _{max} (°C)	HI (mgHC/gTOC)	S ₁ (mg/g)	S ₂ (mg/g)
TA	0.45	439	100	0.04	0.45
TE	4.44	465	37	0.1	1.63
BT	4.47	461	53	0.49	2.38
AA	4.3	440	282	0.96	12.14

TOC, Total Organic Carbon, Wt%; S₁, volatile hydrocarbon (HC) content, mg HC/g rock; S₂, remaining HC generative potential, mg HC/g rock; HI, Hydrogen Index: S₂ × 100/TOC, mg HC/g TOC; T_{max}, temperature at which the maximum amount of organic S₂ hydrocarbons.

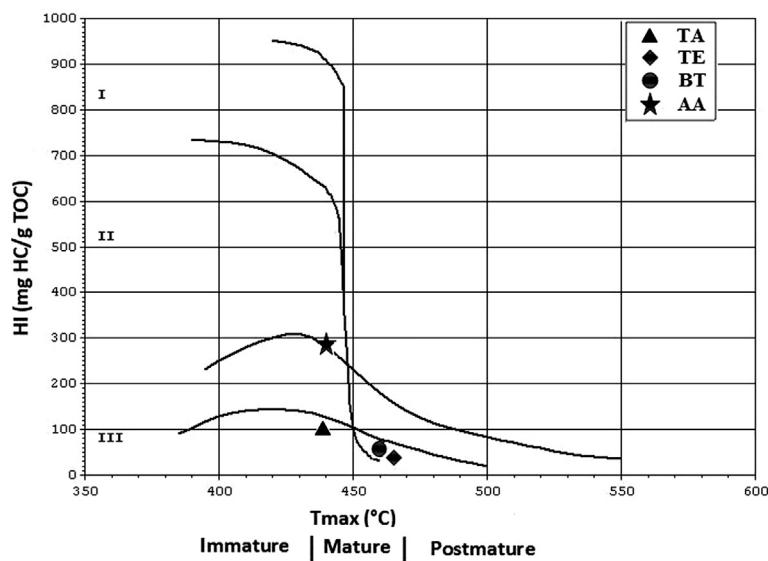


Figure 3 Plot of Hydrogen Index (HI) versus (Rock-Eval) T_{max} values for the samples analyzed showing kerogen quality and thermal maturity stages (diagram from Espitalié et al., 1986).

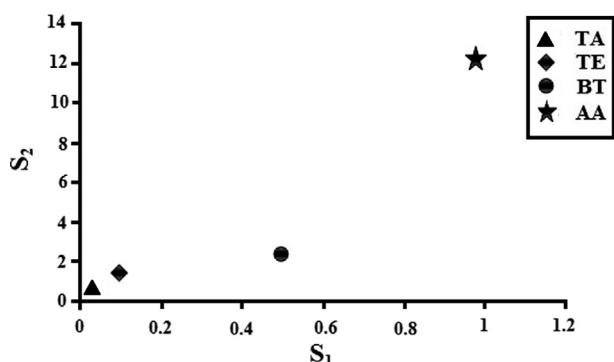


Figure 4 A plot of S₁ vs. S₂ showing a weak positive correlation between S₁ and S₂.

3.2. Flash pyrolysis (Py-GC/MS)

The pyrolysis products of the 4 rock samples (Fig. 5) are mainly aliphatic hydrocarbons identified in the C₁₂–C₃₃ range. It is interesting to notice that the distributions are exactly the same as that observed using the protocol of extraction and

fractionation. This presence of hydrocarbon compounds is very important in AA sample followed by BT sample, then TE, and TA samples.

3.3. Fractionation yields

The results of the bituminous fractionation of the rock samples are shown in Table 2. The TA and TE samples were characterized by the highest amount of polar fraction yields compared to the acid and neutral fractions. The neutral fraction yield is higher in the TE sample than in the TA one. The BT and AA samples were characterized by the upper amount of neutral fraction yields followed by polar fraction yields and the lowest amount of acid fraction yields.

3.4. Chromatographic analysis of the lipids

3.4.1. n-Alkanes

The distribution of the aliphatic hydrocarbons from the neutral fractions is given in Fig. 7. Based on ion extraction, mass of *m/z* 85, *n*-alkanes were detected in the C₁₂–C₃₃ range. The more abundant *n*-alkanes are C₁₆ and C₁₈ for BT, C₁₈ and C₂₄ for TA, C₁₉ and C₂₀ for AA, C₁₆ for TE samples. The distribution of *n*-alkanes can be used as an indicator; although,

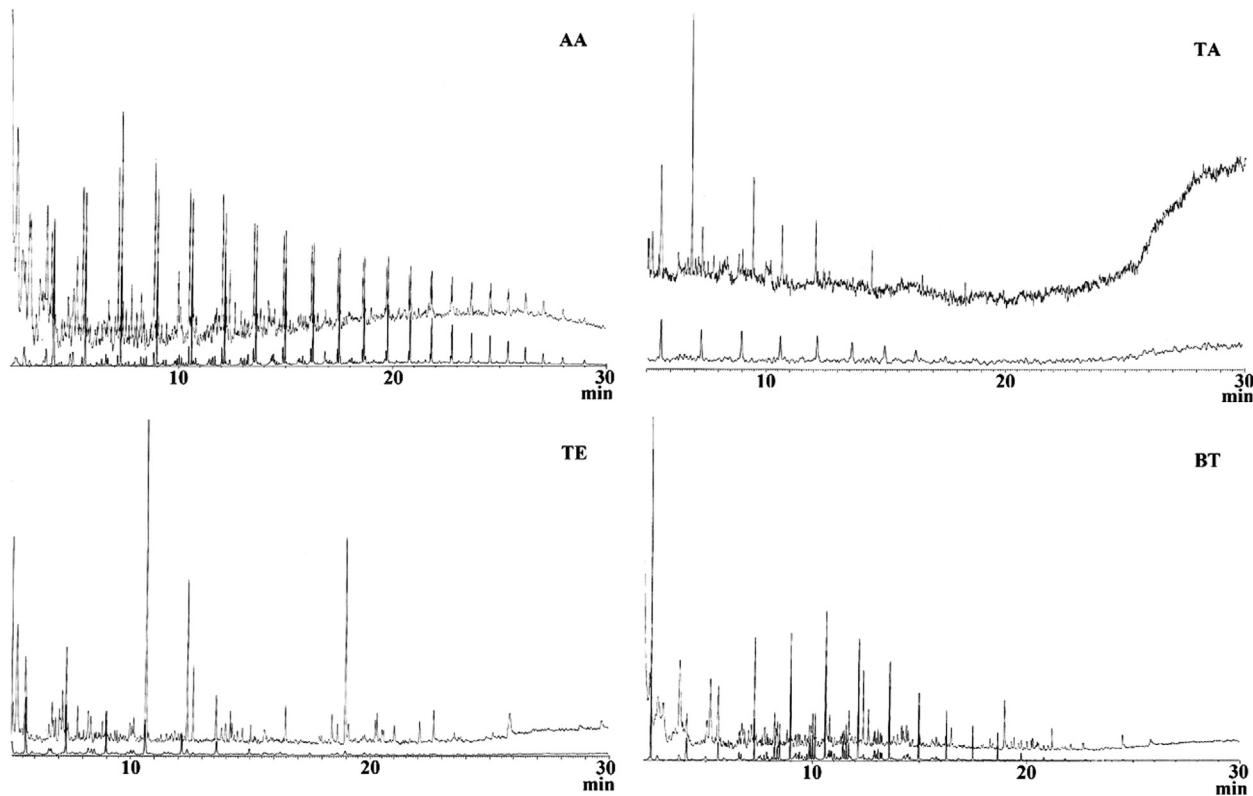


Figure 5 Chromatograms obtained after Py-GC/MS analysis of the bituminous rock samples.

Table 4 Biomarker parameter for extracts of bituminous rock samples studied.

Sample	n-Alkanes				Steranes				Hopane (Terpane)			
	C_{\max}	CPI _{24–34} ^a	Pr/Ph	Waxiness	C ₂₇ (%)	C ₂₈ (%)	C ₂₉ (%)	C ₂₉ 20S/(20S + 20R)	C ₂₉ $\beta\beta$ ($\beta\beta + \alpha\alpha$)	Ts/Tm ^b	Ts/(Ts + Tm)	C ₂₉ /C ₃₀
TA	nC_{24}	1,02	1,03	1,83	26,74	25,24	48,02	0,39	0,86	0,66	0,39	0,93
TE	nC_{16}	0,94	0,60	0,66								
BT	nC_{18}	1,06	1,07	0,79								
AA	nC_{19}	1,01	0,41	1,12	64,07	12,39	23,59	0,34	0,76	1,17	0,54	0,75

^a After Bray and Evans (1961); Waxiness: $\Sigma (n\text{-}C_{21}\text{--}n\text{-}C_{31})/\Sigma (n\text{-}C_{15}\text{--}C_{20})$; Pr/Ph: pristane/phytane.

^b Ts/Tm: trisnorhopanes/trisnorhopanes ratios.

not a very specific one, for organic source of oils (Duan and Ma, 2001). Indeed, the abundant distribution of higher molecular weight alkanes ($\geq C_{20}$) with odd-predominance is characteristic of an organic matter with a plant origin (Kolattudy, 1970; Powell and McKirdy, 1973; Tissot et al., 1977; Tulloch, 1976), whereas the abundant distribution of low molecular weight alkanes ($< C_{20}$) with slight odd-predominance indicates an algal/bacterial origin (Gelpi et al., 1970; Weete, 1976; Tissot and Welte, 1984; Peters and Moldowan, 1993). The chromatograms of the studied samples (Fig. 7) showed a marked predominance of short to long chain *n*-alkanes, which is an indication of organic matter from a marine environment for AA and TE samples while the organic matter of TA and BT samples originates from land or mixed environment (Tissot and Welte, 1978; Ebukanson and Kinghorn, 1986; Murray and Boreham, 1992), which is supported by the results of the Rock-Eval pyrolysis (Fig. 3).

The plot in Fig. 8 allows a better comparison of the distribution of *n*-alkane and *n*-alk-1-ene that was different for the various samples, having some characteristics that deserve attention. The AA, TE and TA samples showed a distribution of *n*-alkane/*n*-alk-1-ene doublets with an even dominance of carbon numbers, whereas the BT sample showed a distribution of *n*-alkane and *n*-alk-1-ene with dominant odd carbon numbers.

3.4.2. Acyclic isoprenoids

Pristane (Pr) and phytane (Ph) are isoprenoid alkanes with 19 and 20 carbon atoms, respectively. The pristane to phytane ratio (Pr/Ph) is an indicator of depositional environment and source of organic matter (Maxwell et al., 1972, 1973; Didyk et al., 1978; Brooks and Smith, 1969; Powell and Makriday, 1973; Chandra et al., 1994; Large and Gize, 1996). These early workers assumed that both pristane and phytane were derived

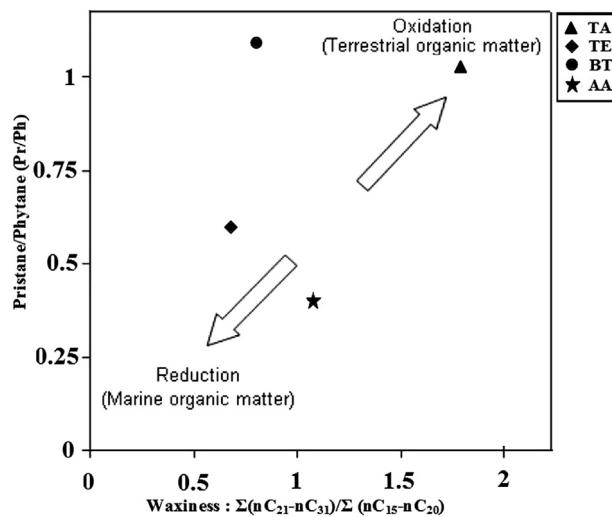


Figure 6 Cross plots of Pr/Ph versus waxiness $\Sigma(n\text{-C}_{21}\text{-n-C}_{31})/\Sigma(n\text{-C}_{15}\text{-n-C}_{20})$ for the studied samples.

from the phytol side chain of chlorophyll. More recently, it has been shown that pristane can be derived from α -tocopherol and phytane from the bis-phytanyl ethers which occur in archaeabacteria (Philp, 1994). According to Cooper (1990), pristine and phytane are derived from the chlorophyll of higher plants, algae and photosynthetic bacteria and from archaeabacteria. A Pr/Ph ratio > 3.0 indicates oxidizing conditions, low values of Pr/Ph ratio (< 0.8) indicate algae/bacteria origin (anoxic conditions), and values between 0.8 and 3.0

suggest intermediate conditions (suboxic conditions) (Ten Haven et al., 1987; Amane and Hideki, 1997; Sarmiento and Rangel, 2004; Basent et al., 2005). The existence of various precursors therefore indicates that the Pr/Ph ratio should be used with care. For our samples (Table 4), the Pr/Ph ratios are < 0.6 for AA sample and 0.60 for TE sample, indicating that these samples derived from source rocks deposited under anoxic conditions, whereas the Pr/Ph ratios for the others samples TA and BT are 1.03 and 1.07 indicating that these samples derived from source rocks deposited under suboxic conditions. The degree of waxiness $(\Sigma(n\text{-C}_{21}\text{-n-C}_{31})/\Sigma(n\text{-C}_{15}\text{-n-C}_{20}))$ (Table 4) that was used as an environmental source parameter (Connan and Cassou, 1980) and the relationship with the Pr/Ph ratio (Fig. 6) confirm that AA and TE samples originate from marine organic matter; whereas, TA and BT samples are derived from terrestrial or mixed organic matter.

3.4.3. Carbon Preference Index (CPI)

The CPI value is a parameter that is influenced by maturity and by the type of organic matter (Tissot and Welte, 1984). The CPI indices initially introduced by Bray and Evans (1961) are the most used, there is no harmonization between the authors on how to perform intercourse. The odd carbon preference is characteristic of oils derived from source rocks deposited in non-marine depositional environments (Moldowan et al., 1985). In contrast, Palacas et al. (1984) concluded that an even numbered *n*-alkane preference is commonly observed in bitumens and oils derived from carbonate or evaporate rocks. In these studied samples, the CPI values calculated in the range *n*C₂₄–*n*C₃₄ (after Bray and Evans,

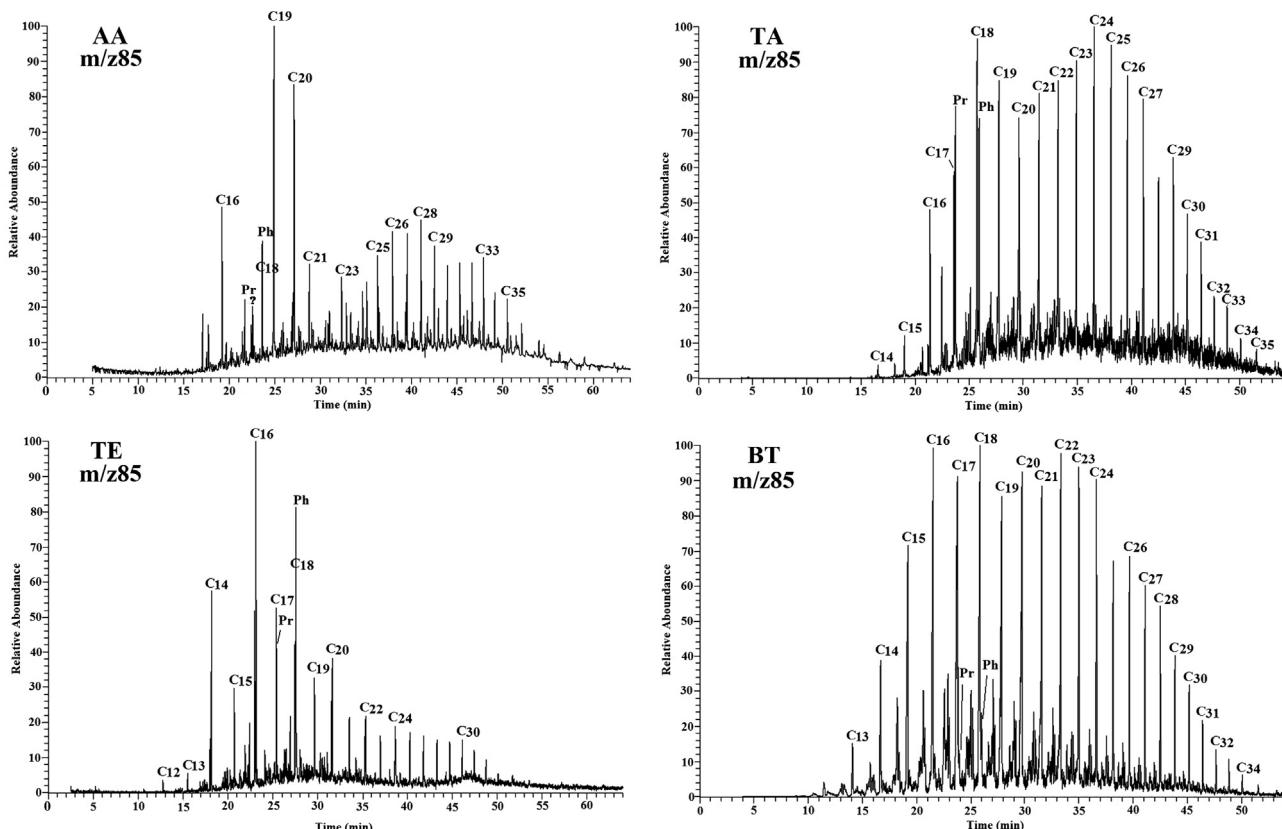


Figure 7 Chromatograms of the saturated hydrocarbon fractions of the bituminous rock samples.

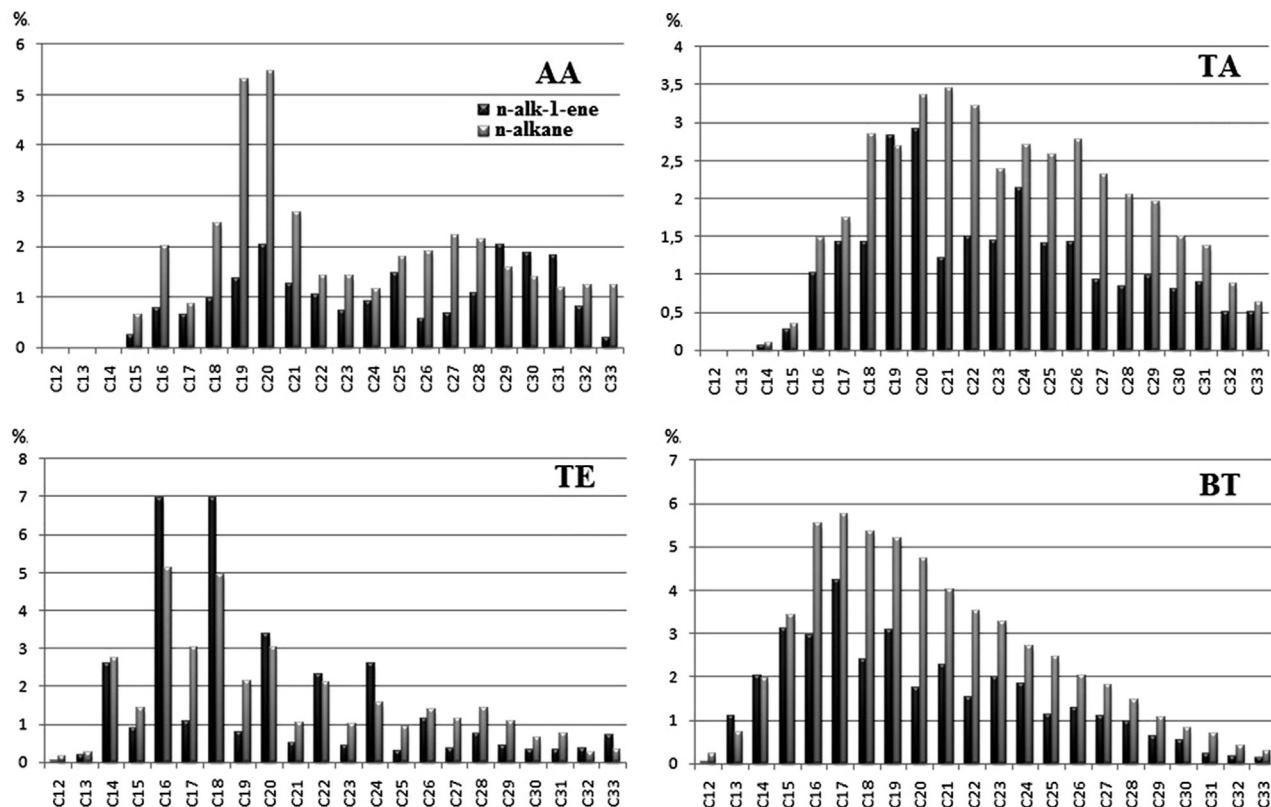


Figure 8 Relative abundance of *n*-alkane and *n*-alk-1-ene in the bituminous rock samples.

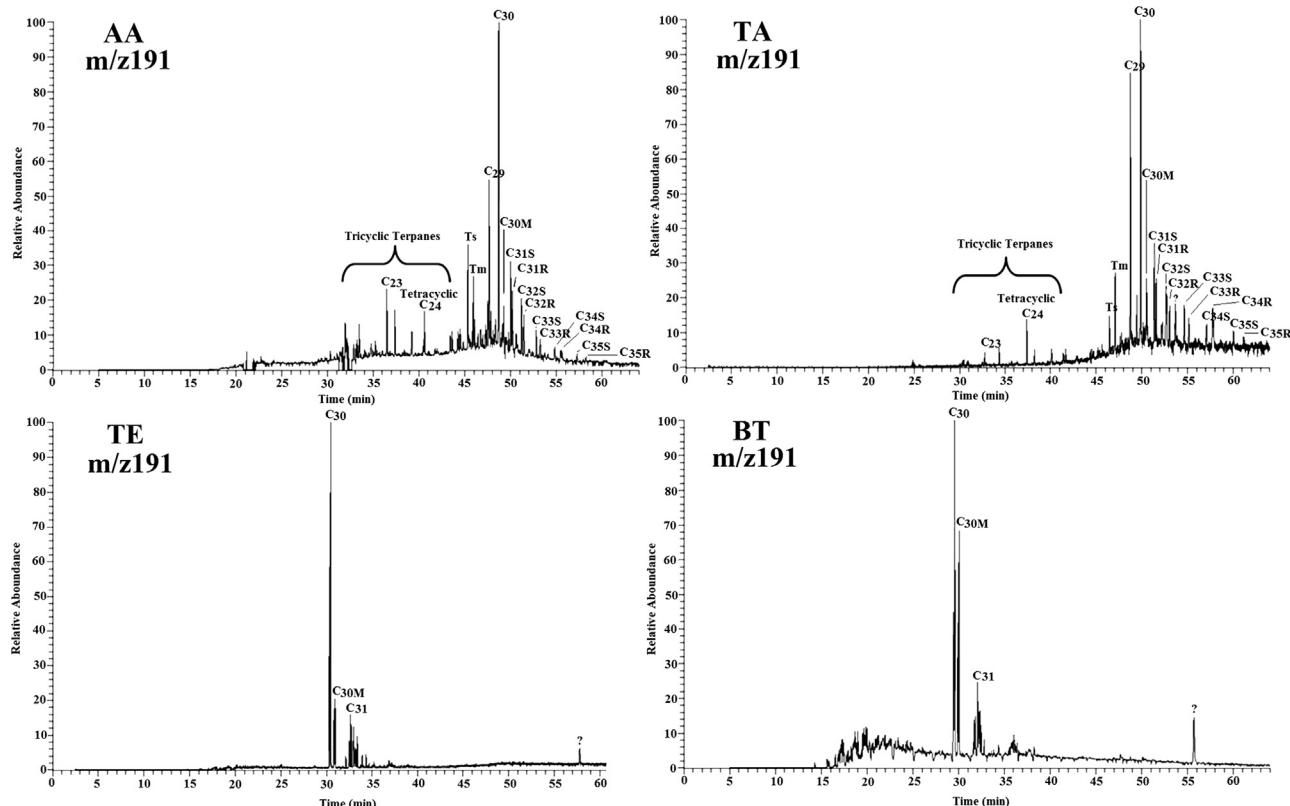


Figure 9 m/z 191 mass-chromatograms of saturated hydrocarbons of bituminous rock samples studied.

Table 5 Peak assignments for alkane hydrocarbons m/z 191 mass chromatograms (Hopane) and m/z 217 mass chromatograms (sterane, diasterane).

Peak	Compound
Ts	18 α (H),22,29,30-trisnorneohopane
Tm	17 α (H),22,29,30-trisnorhopane
C29	17 α ,21 β (H)-nor-hopane
C30	17 α ,21 β (H)-hopane
C30M	17 β ,21 α (H)-moretane
C31S	17 α ,21 β (H)-homohopane (22S)
C31R	17 α ,21 β (H)-homohopane (22R)
C32S	17 α ,21 β (H)-homohopane (22S)
C32R	17 α ,21 β (H)-homohopane (22R)
C33S	17 α ,21 β (H)-homohopane (22S)
C33R	17 α ,21 β (H)-homohopane (22R)
C34S	17 α ,21 β (H)-homohopane (22S)
C34R	17 α ,21 β (H)-homohopane (22R)
C35S	17 α ,21 β (H)-homohopane (22S)
C35R	17 α ,21 β (H)-homohopane (22R)
dC(no) $\beta\alpha S$	13 β ,17 α (H)-diasteranes (20S)
dC(no) $\beta\alpha R$	13 β ,17 α (H)-diasteranes (20R)
dC(no) $\alpha\beta S$	13 α ,17 β (H)-diasteranes (20S)
dC(no) $\alpha\beta R$	13 α ,17 β (H)-diasteranes (20R)
C(no) $\alpha\alpha\alpha S$	5 α ,14 α (H),17 α (H)-steranes (20S)
C(no) $\alpha\beta\beta R$	5 α ,14 β (H),17 β (H)-steranes (20R)
C(no) $\alpha\beta\beta S$	5 α ,14 β (H),17 β (H)-steranes (20S)
C(no) $\alpha\alpha\alpha R$	5 α ,14 α (H),17 α (H)-steranes (20R)

No: number of carbon.

1961) are 1.02, 0.94, 1.06, and 1.01 for TA, TE, BT and AA samples, respectively (Table 4), showing neither even nor odd carbon preference, as an indication of mature samples (Tissot and Welte, 1984).

3.4.4. Terpenic biomarkers

Terpenes are formed by the union of isoprenoid units, the steranes are the most important petroleum hydrocarbons that retain the characteristic structure of the original biological compounds. Tricyclic and tetracyclic hopanes as well as other compounds contribute to the terpane fingerprint (mass chromatogram m/z 191) commonly used to relate oils and source rocks (Seifert and Moldowan, 1979; Hunt, 1996; Peters et al., 2005). The terpane biomarkers present in the saturated hydrocarbon fraction of the studied samples were detected using the characteristic ion extract m/z = 191. Fragmentograms are not similar for both TA and AA samples, contrary to the two other samples (Fig. 9). The assignment of the peaks labeled in Fig. 9 is listed in Table 5. The principal distinct features are tricyclic terpanes, Ts/Tm, Ts/(Ts + Tm) and C₂₉/C₃₀ hopane ratios.

Tricyclic terpanes are members of a useful series of biomarkers for differentiating different types of organic matter and depositional environments (Seifert and Moldowan, 1979; Walples and Machihara, 1991; Andrew et al., 2001; Peters et al., 2005). AA sample has relatively high abundance of the C₂₃ tricyclic terpane and low abundance than the C₂₄ tetracyclic one (Fig. 9), which supports the high contribution from marine material of the source rocks. On the Contrary, the TA sample has high abundance of the C₂₄ tetracyclic and low abundance than the C₂₃ tricyclic (Fig. 9) which supports the high contribution from terrestrial material to the source

rocks (Zumberge, 1987; Burwood et al., 1992; Hanson et al., 2000). In the other samples, the presence of tricyclic terpanes does not seem obvious (Fig. 9).

The Ts/Tm ratio is 0.66 for TA sample and 1.17 for AA sample (Table 4), indicating that the 18 α (H)-trisnorhopane (Tm) is dominant over its counterpart 17 α (H)-trisnorhopanes (Ts) in TA sample, contrary to AA sample. The trisnorhopanes (Ts) and trisnorhopanes (Tm) seem either absent or are present in very minor amounts in the other samples (TE, BT) (Fig. 9). Ts/(Ts + Tm) ratio is one of the indices that has been used for characterization of the source oil (Wang et al., 1998) and evaluation of the thermal maturity (Peters et al., 2005). Higher values indicate higher maturities (Waseda and Nishita, 1998; Seifert and Michael Moldowan, 1978). Ts/(Ts + Tm) values are 0.39, 0.54 for TA and AA samples, respectively (Table 4), suggesting that these sediments are thermally mature.

The studied samples have higher concentrations of C₃₀ than C₂₉ hopane. The C₂₉/C₃₀ 17 α (H) hopane ratio values are 0.93, 0.75, and 0.57 for TA, AA, and TE samples, respectively (Table 4). The ratio cannot be determined for the BT sample. According to the C₂₉/C₃₀ 17 α (H) hopane ratios values (Connan et al., 1986), it seems that the TA sample is more rich in carbonaceous organic matter than the AA and TE samples.

3.4.5. Sterane biomarkers

The transformation of sterols into diagenetic steranes (Mackenzie et al., 1982) is a complex process, yielding the isomers 5 α (H) and 5 β (H), 14 α (H) and 14 β (H) (Seifert and Moldowan, 1979; Mackenzie et al., 1980) the number of carbon atoms being preserved. The distribution of steranes as those of sterols (Huang and Meinschein, 1979) can be used as an indicator of organic input and maturity (Mackenzie and McKenzie, 1983). The different proportions of C₂₇:C₂₈:C₂₉ regular steranes have been proposed as indicative of organic input and maturity (Moldowan et al., 1985; Philp et al., 1991). An abundance of C₂₉ over C₂₇ steranes would suggest a terrestrial source, whereas C₂₇ steranes predominating over C₂₉ steranes would indicate mainly a marine or aquatic source (Lijmbach, 1975; Huang and Meinschein, 1979; Palacas et al., 1984; Gonzalez-Vila, 1995; Hunt, 1995; Peters et al., 2005). The characteristic m/z 217 mass fragmentograms corresponding to the steranes and diasteranes of the representative samples are shown in Fig. 10 and the corresponding chemical structures are given in Table 5. The compounds were identified according to previously reported mass spectra and relative retention times. The AA sample is characterized by the dominance of the C₂₇ sterane (20R, Fig. 10) on the C₂₉ sterane (20R, Fig. 10) (Table 4), which suggests an origin from marine organic matter. The TA sample is characterized by dominance of the C₂₉ sterane (20R, Fig. 10) on the C₂₇ sterane (20R, Fig. 10, Table 4), which indicates an origin from terrestrial organic matter. The steranes diagram (Fig. 11) confirms these assumptions. In addition, the ratio 20S/(20S + 20R) for regular C₂₉ steranes and the $\beta\beta(\beta\beta + \alpha\alpha)$ ratio for C₂₉ are 0.34, 0.76, respectively in AA sample, and 0.39 and 0.86, respectively, in TA samples (Table 4) suggesting that these sediments are thermally mature (Moldowan et al., 1994). A higher degree of maturity and a more pronounced terrigenous source (Petersen et al., 2000; Andrew et al., 2001) is observed for the TA sample compared to the AA sample.

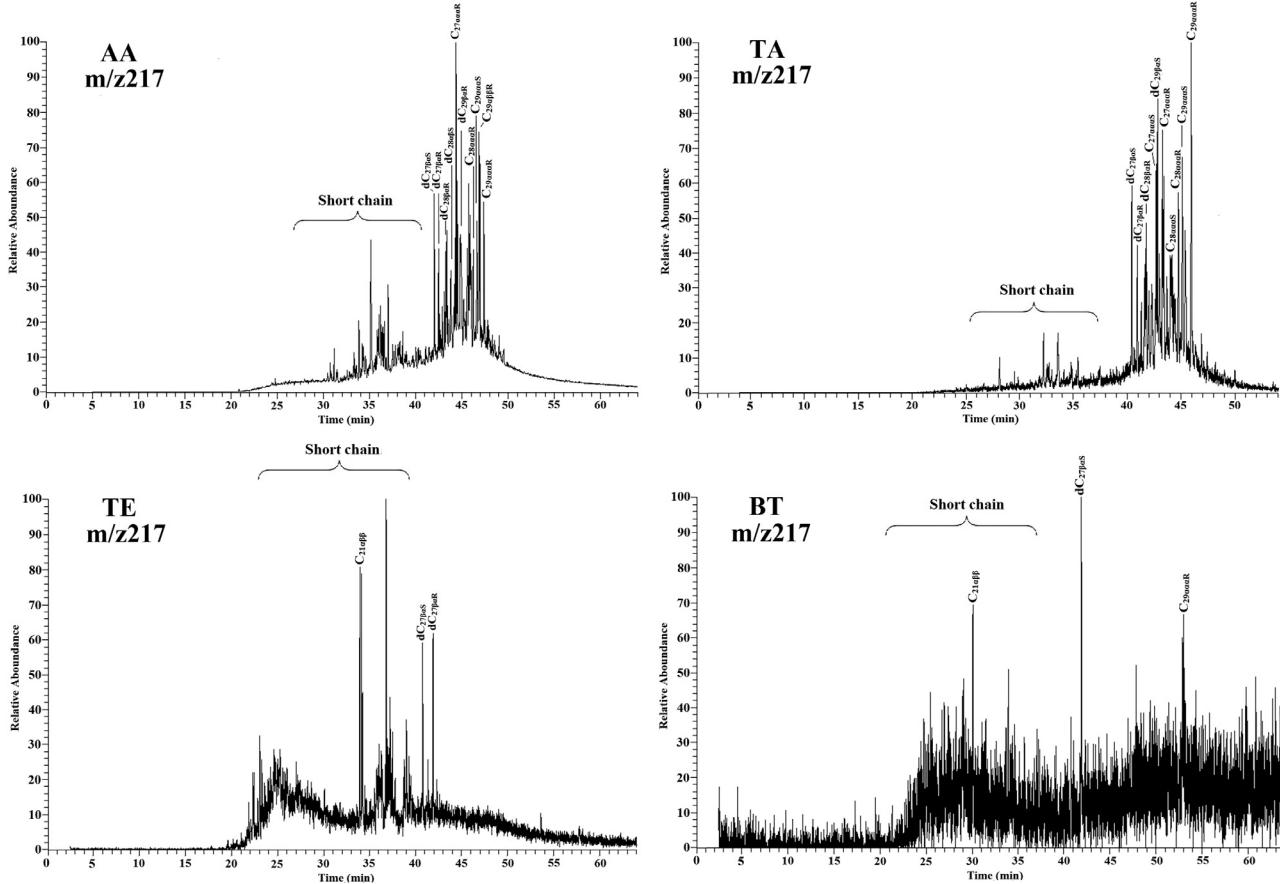


Figure 10 m/z 217 mass-chromatograms of saturated hydrocarbons of bituminous rock samples studied.

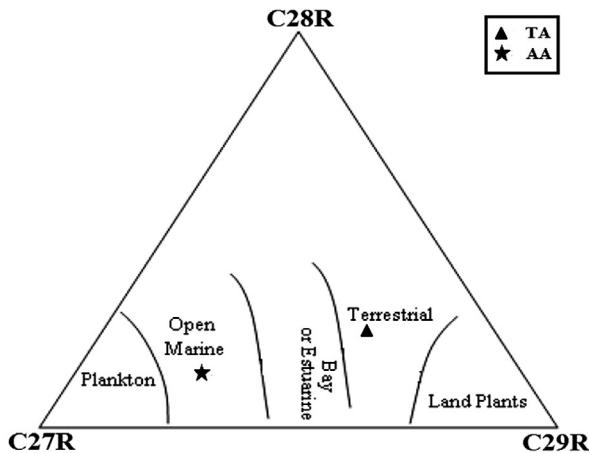


Figure 11 Ternary diagram showing C27–C28–C29 $\alpha\alpha\alpha R$ regular steranes of bituminous rock samples studied.

4. Conclusions

The chromatography study of the Upper Cretaceous bituminous rocks in the Moroccan Rif gives important information about the characterization and classification of organic matter present in these sediments. Using geochemical biomarker parameters related to thermal maturity, organic matter source,

age and depositional environment, the present chromatographic study showed that:

- The samples are generally thermally mature, depending on the geochemical biomarker parameters.
- The AA sample (oil shale) from Arba Ayach site is rich in aliphatic compounds, derived of organic matter from marine, and it has the qualities of a good source rock.
- The TA sample (bituminous marl) from Tangier site is rich in polar compounds, derived of organic matter from terrestrial.
- The TE, BT samples (bituminous phtanite) from Tetouan, Bab Taza sites successively contain aliphatic and polar compounds, but these sediments (bituminous phtanites) are not potential source rocks for hydrocarbons.

This is confirmed by the Rock-Eval pyrolysis results by suggesting Type II, III kerogen for AA, TA samples respectively, and Type IV kerogen for TE, BT samples. Type IV kerogen is poor in hydrogen, therefore inert to generate hydrocarbons (Peters and Cassa, 1994). Additional Rock-Eval pyrolysis results confirmed the thermal maturity for the AA sample. Although, it is contrary for the other samples due to their low S_2 hydrocarbon value ($< 2.5 \text{ mg HC/g rock}$) (Groune et al., 2013).

Acknowledgement

The authors are thankful to the Hassan II Academy of Science and Technology-Rabat (Morocco) for its help to carry out this study.

References

- Amane, W., Hideki, N., 1997. Geochemical characteristics of terrigenous and marine sourced oils in Hokkaido, Japan. *Org. Geochem.* 28, 27–41.
- Amblès, A., Halim, M., Jacquesy, J.C., Vitorovic, D., Ziyad, M., 1994. Characterization of kerogen from Timahdit shale (Y-layer) based on multistage alkaline permanganate degradation. *Fuel* 73, 17–24.
- Andrew, D.H., Bradley, D.R., David, Z.J., Moldowan, M., Ulderico, B., 2001. Upper Oligocene lacustrine source rocks and petroleum systems of the northern qaidam basin, North West China. *Bull. Am. Assoc. Pet. Geol.* 85, 601–619.
- Basant, G.G., Rajendra, S.B., Ashok, K.B., Dinesh, K., Kusum, L.P., Adarsh, K.M., Jagdish, P.G., Gaur, C.D., Nizhat, J.T., 2005. Geochemical characterization an source investigation of oils discovered in Khoraghat–Nambar structures of the Assam-Arakan Basin, India. *Org. Geochem.* 36, 161–181.
- Bray, E.E., Evans, E.D., 1961. Distribution of *n*-paraffins as a clue to recognition of source beds. *Geochim. Cosmochim. Acta* 22, 2–15.
- Brooks, J., Smith, W.J., 1969. The diagenesis of plant lipids during the formation of coal petroleum and natural gas coalification and the formation of oils and gas in the Gippsland basin. *Geochim. Cosmochim. Acta* 33, 1183–1194.
- Burwood, R., Leplat, P., Mycke, B., Paulet, J., 1992. Rifted margin source rock deposition: a carbon isotope and biomarker study of a west African Lower Cretaceous “lacustrine” section. *Org. Geochim.* 19, 41–52.
- Chandra, K., Mishra, C.S., Samanta, U., Gupta, A., Mehrotra, K.L., 1994. Correlation of different maturity parameters in the Ahmedabad–Mehsana block of the Cambay basin. *Org. Geochem.* 21, 313–321.
- Connan, J., Cassou, A.M., 1980. Properties of gases and petroleum liquids derived from terrestrial kerogen at various maturation levels. *Geochim. Cosmochim. Acta* 44, 1–23.
- Connan, J., Bouroullec, J., Dessort, D., Albrecht, P., 1986. The microbial input in carbonate-anhydrite facies of sabkha palaeoenvironment from Guatemala. A molecular approach. In: Leythaeuser, D., Rulkötter, J. (Eds.), *Advances in Organic Geochemistry 1985*, 10. *Org. Geochem.*, pp. 29–50.
- Cooper, B.S., 1990. *Practical Petroleum Geochemistry*. Roberston Scientific Publications, London, pp. 40–48.
- Didyk, B.M., Simoneit, B.R.T., Brassell, S.C., Eglinton, G., 1978. Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. *Nature* 272, 216–222.
- Duan, Y., Ma, L.H., 2001. Lipid geochemistry in a sediment core from Ruergai Marsh deposit (Eastern Qinghai-Tibet Plateau, China). *Org. Geochem.* 32, 1429–1442.
- Durand, B., 1980. Sedimentary organic matter and kerogen. Definition and quantitative importance. In: Durand, B. (Ed.), *Kerogen. Technip, Paris*, pp. 13–34.
- Durand-Delga, M., Kornprost, J., 1985. Carte géologique du Tétouan – Ras Mazari 1/50.000. Notes et Mém. Serv. Géol. Maroc. N° 292.
- Durand-Delga, M., Olivier, P., 1988. Carte géologique du Rif Méloussa 1/50.000. Notes et Mém. Serv. Géol. Maroc. N° 296 (modified).
- Ebukanson, E.J., Kinghorn, R.R.F., 1986. Maturity of organic matter in the Jurassic of southern England and its relation to the burial history of the sediments. *J. Pet. Geol.* 93, 259–280.
- Espitalié, J., Laporte, J.L., Madec, M., Marquis, F., Leplat, P., Paulet, J., Bouteleu, A., 1977. Méthodes rapides de caractérisation des roches mères de leur potentiel pétrolier et de leur degré d'évolution. *Revue de l'Institut Français du Pétrole* 32, 23–42.
- Espitalié, J., Deroo, G., Marquis, F., 1986. Rock-Eval pyrolysis and its applications. Part III. *Revue de l'Institut Français du Pétrole* 41, 73–89.
- Filatov, F., 1970. Estimation géologie et industrielle préliminaire des gisements de schistes bitumineux du Maroc – Rapport SEGM, N 888.
- Gelpi, E., Schneider, H., Mann, J., Oroño, J., 1970. Hydrocarbons of geological significance in microscopic algae. *Phytochemistry* 46, 1663–1671.
- Gonzalez-vila, F.J., 1995. Alkane biomarkers geochemical significance and application in oil shale geochemistry. In: Snape, C. (Ed.), *Composition, Geochemistry and Conversions of Oil Shales*. Kluwer Academic Publishers, pp. 51–68.
- Groune, K., Halim, M., Benmakhlouf, M., Arsalane, S., Lemee, L., Ambles, A., 2013. Organic geochemical and mineralogical characterization of the Moroccan Rif bituminous rocks. *J. Mater. Environ. Sci.* 4 (4), 472–481.
- Halim, M., 1993. Etude de la matière organique sédimentaire, Gisements de Timahdit et Tarfaya (Thèse de Doctorat de Sciences), Université Mohamed V, Rabat, pp. 33.
- Hanson, A.D., Zhang, C., Moldowan, J.M., Liang, D.G., Zhang, B.M., 2000. Molecular organic geochemistry of the Tarim Basin, north-west China. *Am. Assoc. Pet. Geol. Bull.* 84, 1109–1128.
- Huang, W.Y., Meinschein, W.G., 1979. Sterols as source ecological indicators. *Geochim. Cosmochim. Acta* 43, 739–745.
- Hunt, J.M., 1995. *Petroleum Geochemistry and Geology*, 2nd ed. W.H. Freeman and Company, New York, NY.
- Hunt, J.H., 1996. *Petroleum Geochemistry and Geology*, 2nd ed. W.H. Freeman and Company, New York, p. 743.
- Hutton, A.C., 1987. Petrographic classification of oil shales. *Int. J. Coal Geol.* 8 (3), 203–231.
- Jabobker, A., 2003. Maîtrise de la manipulation du Rock Eval 6 standard et l'utilisation de ses logiciels associés, N 44/4 à la documentation du l'ONHYM, Rabat.
- Jabobker, A., 2004. Rapport de stage de formation sur la manipulation du Rock Eval 6 Standard et l'utilisation de ses logiciels associés (2 au 11 Avril en France), N 02495 à la documentation du l'ONHYM, Rabat.
- Kolattudy, P.E., 1970. Plant waxes. *Lipids* 5, 259–275.
- Kornprost, J., Wildi, W., Nold, M., Gutnie, M., Lespinasse, P., 1980. Carte géologique du Rif Bab Taza 1/50.000. Notes et Mém. Serv. Géol. Maroc. N 288.
- Large, D.J., Gize, A.P., 1996. Pristane/phytane ratios in the mineralized Kupferschiefer of the Fore-Sudetic Monocline, Southwest Poland. *Ore Geol. Rev.* 11, 89–103.
- Larter, S.R., Horsfield, B., 1993. In: Engel, M.H., Macko, S.A. (Eds.), *Organic Geochemistry*. Plenum Press, New York, pp. 271–287.
- Lijmbach, G.W.M., 1975. On the origin of petroleum. *Proc. 9th World Pet. Cong.* 2, 357–369.
- Mackenzie, A.S., McKenzie, D., 1983. Isomerization and aromatization of hydrocarbons in sedimentary basins formed by extension. *Geol. Mag.* 120, 417–470.
- Mackenzie, A.S., Patience, A.L., Maxwell, J.R., Vandebroucke, M., Durand, B., 1980. Molecular parameters of maturation in the Toarcian Shales, Paris Basin, France. I. Changes in the configurations of acyclic isoprenoid alkanes, steranes and triterpanes. *Geochim. Cosmochim. Acta* 44, 1709–1721.
- Mackenzie, A.S., Brassell, S.C., Eglinton, G., Maxwell, J.R., 1982. Chemical Fossils: the geological fate of steroids. *Science* 217, 491–504.
- Maxwell, J.R., Cox, R.F., Akman, R.G., Hooper, S.N., 1972. In: Von Goertner, H.R., Wehner, H. (Eds.), *Advances in Organic Geochemistry*. Pergamon Press, p. 277.
- Maxwell, J.R., Cox, R.F., Eglinton, G., Pillinger, C.T., 1973. *Geochim. Cosmochim. Acta* 37, 297.

- McCarthy, R.D., Duthie, A.H., 1962. A rapid quantitative method for the separation of free fatty acids from other lipids. *J. Lipid Res.* 3, 117–119.
- Moldowan, J.M., Seifert, W.K., Gallegos, E.J., 1985. Relationship between petroleum composition and depositional environment of petroleum source rocks. *Am. Assoc. Pet. Geol. Bull.* 69, 1255–1268.
- Moldowan, J.M., Dahl, J., Huizinga, B.J., Fago, F.J., Hickey, L.J., Peakman, T.M., Taylor, D.W., 1994. The molecular fossil record of oleanane and its relation to angiosperms. *Science* 265, 768–771.
- Murray, A.P., Boreham, C.J., 1992. Organic Geochemistry in Petroleum Exploration. Australian Geological Survey Organization, Canberra, p. 230.
- Nejma, M., 1989. Contribution à la mise en valeur de la roche à kérogène de Timahdit (Thèse de Doctorat de Sciences), Université Mohamed V, Rabat, pp. 689–692.
- Palacas, J.G., Anders, D.E., King, J.D., 1984. South Florida basin-prime example of carbonate source rocks of petroleum. In: Palacas, J.G. (Ed.), Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks AAPG, 18. Studies in Geology, pp. 71–96.
- Peters, K.E., Cassa, M.R., 1994. Applied Source Geochemistry. In: Magoon, L.B., Dow, W.G. (Eds.), . In: The Petroleum System—from Source to Trap, 70. AAPG Bull., p. 329.
- Peters, K.E., Moldowan, J.M., 1993. The biomarker guide: interpreting molecular fossils. In: Petroleum and Ancient Sediments. Prentice Hall, New Jersey, p. 363.
- Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. The Biomarker Guide: Biomarkers and Isotopes in Petroleum Systems and Earth History, second ed. Cambridge University, pp. 476–625.
- Petersen, H.I., Andsbjerg, J., Bojesen-Koefoed, J.A., Nytoft, H.P., 2000. Coal-generated oil: source rock evaluation and petroleum geochemistry of the lulita oil field, Danish North Sea. *Pet. Geol.* 23, 55–99.
- Philp, R.P., Fan, P., Lewis, C.A., Li, J., Zhu, H., Wang, H., 1991. Geochemical characteristics of oils from Chaidamu, Shanganning and Jianghan basins, China. *J. Southeast Asian Earth Sci.* 5, 351–358.
- Philp, R.P., 1982. Application of pyrolysis–GC and pyrolysis–GC–MS to fossil fuel research. *Trends Anal. Chem.* 1 (10), 237–241.
- Philp, R.P., 1994. Geochemical characteristics of oil derived predominantly from terrigenous source materials. In: Scott, A.C., Fleet, A.J. (Eds.), Coal and Coal-Bearing Strata as Oil Prone Source Rocks?, Geol Soc. Special Publication 77. The Geological Society, London, pp. 71–91.
- Powell, T.G., Makriday, D.M., 1973. Relationships between ratio of pristine to Phytane, crude oil composition and geological environments in Australia. *Nature* 243, 37–39.
- Powell, T., McKirdy, D.M., 1973. The effect of source material, rock type and diagenesis on the n-alkane content of sediments. *Geochim. Cosmochim. Acta* 37, 623–633.
- Saadi, M., Bouhaouli, A., Hilali, E.A., Ider, E.H., Ralhali, T., 1981. Les roches bitumineuses marocaines, Numéro. Spécial Consacré aux schistes bitumineux au Maroc, Géologie et Énergie, Ministère de l'Énergie et des Mines, N 50.
- Sarmiento, L.F., Rangel, A., 2004. Petroleum systems of the Upper Magdalena Valley, Colombia. *Mar. Pet. Geol.* 21, 373–391.
- Seifert, W.K., Michael Moldowan, J.M., 1978. Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. *Geochim. Cosmochim. Acta* 42, 77–95.
- Seifert, W.K., Moldowan, J.M., 1979. The effect of biodegradation on steranes and terpanes in crude oils. *Geochim. Cosmochim. Acta* 43, 111–126.
- Ten Haven, H.L., De Leeuw, J.W., Rullkötter, J., Sinnighe, D.J.S., 1987. Restricted utility of the pristane/phytane ratio as a palaeoenvironmental indicator. *Nature* 330, 641–643.
- Tissot, B., Welte, H.D., 1978. Petroleum Formation and Occurrence, A New Approach to Oil and Gas Exploration. Springer Verlag, p. 538.
- Tissot, B., Welte, D., 1984. Petroleum Formation and Occurrence, 2nd ed. Springer Verlag, Heidelberg, p. 699.
- Tissot, B., Pelet, R., Roucaché, J., Combaz, A., 1977. Utilisation des alcanes comme fossiles géochimiques indicateurs des environnements géologiques. In: Campos, R., Gonçalves, J. (Eds.), Advances in Organic Geochemistry, 1975. Enadimsa, Madrid, pp. 117–154.
- Tulloch, A.P., 1976. Chemistry of waxes of higher plants. *Chem. Biochem. Nat. Waxes*, 235–287.
- Walples, D.W., Machihara, T., 1991. Biomarkers for geologists American association of petroleum geologists methods in exploration series, No. 9, p. 91.
- Wang, Z.D., Fingas, M., Blenkinsopp, S., Sergy, G., Landriault, M., Sigouin, L., Lambert, P., 1998. Study of the 25-year-old Nipisi oil spill: persistence of oil residues and comparisons between surface and subsurface sediments. *Environ. Sci. Technol.* 32, 2222–2232.
- Waseda, A., Nishita, H., 1998. Geochemical characteristics of terrigenous and marine-sourced oils in Hakkaido, Japan. *Org. Geochem.* 28 (1/2), 27–41.
- Weete, J.D., 1976. Algal and fungal waxes. *Chem. Biochem. Nat. Waxes*, 349–418.
- Yen, T.F., 1976. In: Chilingarian, G.V. (Ed.). In: Yen, T.F., Chilingarian, G.V. (Eds.), Introduction to Oil Shales//Oil Shale. Elsevier, Amsterdam, pp. 1–12.
- Zumberge, J.E., 1987. Terpenoid biomarker distributions in low maturity crude oils. *Org. Geochem.* 11, 479–496.